

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
20 September 2001 (20.09.2001)

PCT

(10) International Publication Number  
**WO 01/68572 A1**

(51) International Patent Classification<sup>7</sup>: **C07C 11/107**,  
2/32

Sant' Angelo Lodigiano (IT). **PROTO, Antonio** [IT/IT];  
Via Fara, 59, I-28100 Novara (IT).

(21) International Application Number: PCT/EP01/02827

(74) Agents: **DE GREGORI, Antonella** et al.; Ing. Barzanò  
& Zanardo, Milano S.p.A., Via Borgonuovo, 10, I-20121  
Milan (IT).

(22) International Filing Date: 12 March 2001 (12.03.2001)

(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,  
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,  
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,  
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,  
TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
MI2000A000546 17 March 2000 (17.03.2000) IT

(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

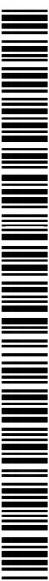
(72) Inventors; and

Published:

(75) Inventors/Applicants (for US only): **SANTI, Roberto**  
[IT/IT]; Viale Piazza d'Armi, 24 F, I-28100 Novara (IT).  
**ROMANO, Anna, Maria** [IT/IT]; Via Ricci, 3, I-28100  
Novara (IT). **GRANDE, Manuela** [IT/IT]; Via N. Sauro,  
47, I-13100 Vercelli (IT). **SOMMAZZI, Anna** [IT/IT];  
Piazza Mazzini, 10, I-16038 Santa Margherita Ligure  
(IT). **MASI, Francesco** [IT/IT]; Via Galvani, 7, I-26866

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 01/68572 A1**

(54) Title: PROCESS FOR THE PREPARATION OF 1-HEXENE

(57) Abstract: Process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene in the presence of a catalyst comprising a vanadium complex having the formula: (arene)<sub>2</sub>VX wherein the term arene represents benzene or mono-, di-, or tri-alkylsubstituted benzene, V is a vanadium ion with a low oxidation state, and X is an anion selected from Cl, Br and I halide ions, or from non-coordinated anions such as B(Ar)<sub>4</sub><sup>-</sup>, AlCl<sub>4</sub><sup>-</sup>, carboxylates and sulfonates.

## PROCESS FOR THE PREPARATION OF 1-HEXENE

The present invention relates to a process for the preparation of 1-hexene by the oligomerization of ethylene in the presence of vanadium complexes with a low oxidation state.

The possibility of preparing olefins with a double terminal bond by means of the oligomerization of lower olefins, for example 1-hexene by the trimerization of ethylene, is already known: for example United States patent 4,668,838 describes a process involving the use of a catalyst which comprises the reaction product between a chromium compound, a hydrocarbon derivative of partially hydrolyzed aluminum and a ligand-donor compound; European patent application 416,304 involves, in the process in question, the use of a catalytic system comprising a pyrrolidic compound of chromium and a compound of aluminum; European patent application 537,609 relates to the process

of interest which is carried out in the presence of a catalyst consisting of a complex of chromium with a polydentate ligand and an aluminoxane.

In addition to the above references, others  
5 can be cited relating to the use of catalytic systems based on compounds of chromium; preparation processes of 1-hexene by the oligomerization of ethylene in the presence of these catalytic systems, however, seem to have various drawbacks  
10 such as, for example, insufficient activity of the catalyst or difficulty in its preparation or the low selectivity with respect to the desired product.

The Applicant has now found that it is possible to effect the synthesis of 1-hexene by the oligomerization of ethylene using a process which overcomes all the disadvantages which negatively characterize analogous processes described in the state of the art above, and which consequently  
20 seem to have all the necessary industrial requisites.

The object of the invention, according to the present patent application, therefore relates to a process for the preparation of 1-hexene  
25 which consists in subjecting ethylene to oli-

gomerization in the presence of a catalyst comprising a vanadium complex with a low oxidation state selected from those included in the following formula:

## 5 (arene)<sub>2</sub>VX

wherein the term arene represents benzene or mono-, di-, or tri-alkylsubstituted benzene, V is a vanadium ion with a low oxidation state, and X is an anion such as Cl, Br, I, non-coordinated anions such as  $B(Ar)_4^-$ ,  $AlCl_4^-$ , carboxylates, sulfonates.

The following complexes have proved to be particularly advantageous:

### bis-(mesitylene)-vanadium trifluoroacetate

15 bis-(mesitylene)-vanadium-tetraphenylborate

### bis-(mesitylene)-vanadium-iodide

bis-(mesitylene)-vanadium-tetrachloroaluminate.

Vanadium arenes are already known in the art and can be prepared for example according to the indications, which form an integral part of the present invention, contained in the articles of E.O. Fischer and U.S. Kogler, Chem. Ber. 90, 250 (1957), and F. Calderazzo, Inorg. Chem., 3, 810 (1964): for example according to the schemes of Table 1.

In accordance with a wider aspect of the process of the present invention, these vanadium complexes can be used for the oligomerization of olefins other than ethylene, such as, for example, propylene, 1-butene, etc.: the reason the Applicant has decided to limit the description of the invention to the preparation of 1-hexene alone is simply because of the specific industrial interest in the production of this compound: any expert in the field will be able to understand from this description how to effect the oligomerization reaction starting from olefins other than ethylene, this process being included, however, in the scope of the invention according to the present patent application.

The oligomerization reaction of ethylene, according to the process of the present invention is carried out in the absence of co-catalysts, in the presence of the above vanadium compound alone or in the presence of the vanadium compound and a heterocyclic compound selected from pyrrole and derivatives.

When this heterocyclic compound is adopted, it is used in a ratio, with respect to the vanadium complex, ranging from 1 to 20: heterocyclic

compounds which can be advantageously used are pyrroles, pyrazoles, phenanthroline, pyridine and other mono and polynitrogenated derivatives.

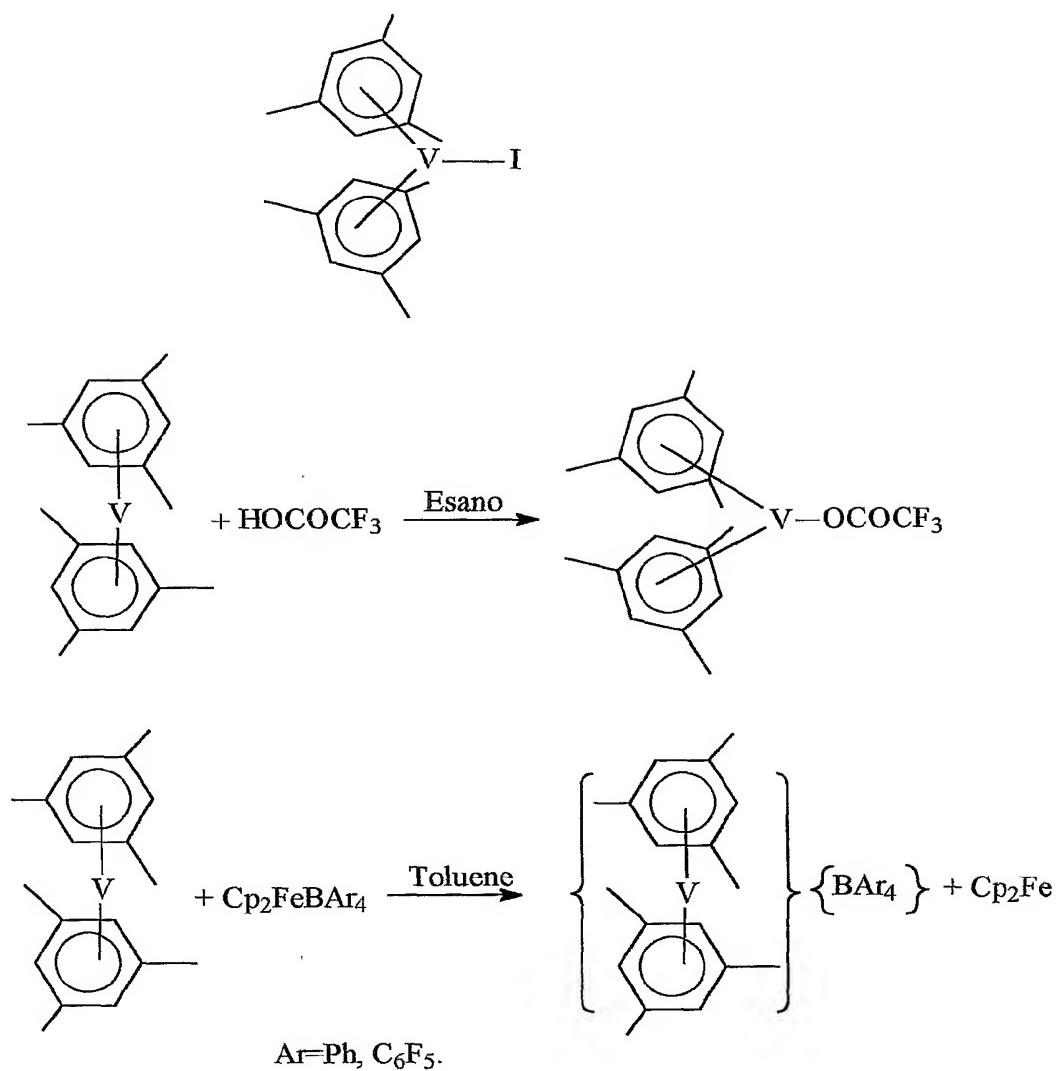
The oligomerization reaction of ethylene,  
5 according to the present invention, is carried out in the presence of a solvent which is normally selected from aromatic hydrocarbons and cycloaliphatic hydrocarbons: of these, the use of toluene and cyclohexane has proved to be particu-  
10 larly advantageous.

The reaction is carried out at a temperature ranging from 0 to 150°C, preferably from 25 to 60°C, and at a pressure ranging from 1 to 100 atm., preferably from 1 to 50 atmospheres. The  
15 reaction time is normally less than 36 hours, preferably from 1 to 24 hours. At the end of the reaction, 1-hexene can be separated and recovered from the reaction mixture using techniques well known to experts in the field.

20 Further details are evident from the following operative examples which are provided for a better illustration of the present invention without limiting its scope however in any way.

Table I

## VANADIUM COMPLEXES



**Example 1: Synthesis of V(mes)<sub>2</sub>(OCOCF<sub>3</sub>)**

1.723 g of V(mes)<sub>2</sub> (5.9 mmoles) and 50 ml of anhydrous and degassed n-hexane are charged under argon into a 250 ml test-tube. 0.44 ml of anhydrous trifluoroacetic acid CF<sub>3</sub>COOH (5.9 mmoles) are added to the brown solution. A brown precipitate is formed which, after 4 hours, is filtered and washed with hexane 6 times. The brown, pump-dried solid weighs 1.2 g (yield 52%).

10 **Example 2: Synthesis of ferrocene tetraphenyl borate Cp<sub>2</sub>Fe(BPh<sub>4</sub>)**

1.13 g of ferrocene Cp<sub>2</sub>Fe (MW = 186; 6.10 mmoles) are charged into a 100 ml flask and 10 ml of H<sub>2</sub>SO<sub>4</sub> at 96% are slowly added dropwise. There is a substantial development of heat. 2.6 g of Na(BPh<sub>4</sub>) (MW = 342; 7.63 mmoles) dissolved in 25 ml of water are slowly added dropwise to the blue solution, Cp<sub>2</sub>Fe(HSO<sub>4</sub>). A blue precipitate is formed, which is filtered and washed with ethanol (5 x 10 ml), followed by ethyl ether (5 x 10 ml) and finally dried for a whole night with a vacuum pump and subsequently on P<sub>2</sub>O<sub>5</sub>.

20 **Example 3: Synthesis of Vanadium bis-(mesitylene) tetra phenyl borate**  
25 **V(mes)<sub>2</sub>(BPh<sub>4</sub>)**

0.350 g of  $\text{Cp}_2\text{Fe}(\text{BPh}_4)$  (MW = 505; 0.7 mmoles) and 0.201 g of  $\text{V}(\text{mes})_2$  (MW = 291; 0.7 mmoles) are charged under argon into a 100 ml test-tube containing 30 ml of anhydrous toluene. The mixture 5 is left under stirring for about 4 hours; the dark solid product is filtered and dried. 0.410 g of product are obtained (yield: 96%).

#### **Example 4**

36 mg of  $\text{V}(\text{mes})_2(\text{OCOCF}_3)$  (MW = 404; 0.089 10 mmoles) are charged under argon into a 100 ml three-necked flask. 20 ml of anhydrous and de-gassed toluene are added. The resulting brown solution under ethylene becomes lighter. It is left at 45°C for 24 hours. The absorption buret registers an ethylene consumption equal to 500 ml. 15 1 ml of the solution is removed, 1 ml of a solution of  $\text{Br}_2$  in  $\text{CCl}_4$  is added and GC analysis is effected.

0.51/22.4 (l/mol) = 0.0223 moles of ethylene used  
20 up

Activity: 250.5 moles of ethylene/V moles

Selectivity: 56% to 1-hexene

#### **Example 5**

81 mg of  $\text{V}(\text{mes})_2(\text{OCOCF}_3)$  (MW = 404;  $2 \cdot 10^{-4}$  25 mmoles) are charged under argon into a 250 ml

three-necked flask. 30 ml of anhydrous and degassed toluene are added. The brown solution under ethylene becomes lighter. After 10 minutes an absorption equal to 67 ml of ethylene is obtained. After 1 hour, as there no longer seems to be any more absorption, 0.080 ml of 2,5-dimethylpyrrole (0.787 mmoles) are added, which causes a further ethylene absorption equal to 33 ml. The green solution, after a night at room temperature, becomes brown again and is analyzed via GC.

0.11/22.4 (l/mol) = 0.00446 moles of ethylene used up

Activity: 22.26 moles of ethylene/vanadium mole

Selectivity: 55% to 1-hexene

15 **Example 6**

56 mg of V(mes)<sub>2</sub>(OCOCF<sub>3</sub>) (MW = 404; 0.138 mmoles) are charged under argon into a 100 ml three-necked flask. 0.042 ml of 2,5-dimethylpyrrole (0.408 mmoles) are added to 20 ml of distilled and degassed cyclohexane. The orange solution under ethylene darkens. It is left at 50°C for 5 hours; after 3 hours the solution is green and has absorbed 70 ml of ethylene.

GC analysis is effected.

25 0.071/22.4 (l/mol) = 0.003125 moles of ethylene

used up

Activity: 22.54 moles of ethylene/vanadium mole

Selectivity: 46% to 1-hexene

**Example 7**

5        64 mg of  $V(\text{mes})_2\text{B}(\text{Ph})_4$  (MW = 610;  $1.04 \cdot 10^{-4}$  moles) are charged under argon into a 100 ml three-necked flask. The mixture is dispersed in 30 ml of anhydrous toluene. The reddish-brown suspension under ethylene darkens. It is left at  
10 room temperature for 20 hours. After this period of time a black suspension is formed.

In 10 minutes, 70 ml of ethylene are absorbed. It is injected into GC.

0.071/22.4 (l/mol) = 0.00315 moles of ethylene  
15 used up

Activity: 29.8 moles of ethylene/vanadium mole

Selectivity: 66% to 1-hexene

**Example 8**

0.2 ml of  $V(\text{mes})_2$  at 6% in hexane (MW = 291;  
20         $4.12 \cdot 10^{-5}$  moles) in 20 ml of degassed and anhydrous toluene are charged under argon into a 100 ml test-tube. 21 mg of  $\text{Cp}_2\text{Fe}(\text{BPh}_4)$  (MW = 505;  $4.12 \cdot 10^{-5}$  moles) are added to the orange solution. The orange solution is diluted up to 100 ml with  
25 toluene, charged into a Buchi 300 ml glass auto-

clave and is put under 7 bars of ethylene and maintained at room temperature for 1 hour. It is observed that as ethylene is absorbed, the solution becomes turbid. The autoclave is degassed 5 and the contents discharged without diluting. 1 ml of the solution is removed, 1 ml of a solution of Br<sub>2</sub> in CCl<sub>4</sub> is added and injected into GC: only 1-hexene is present.

Activity: 605 moles of ethylene/V mole

10 Selectivity: 99% to 1-hexene

### Example 9

30 mg of V(mes)<sub>2</sub>I (MW = 418; 7.17·10<sup>-5</sup> moles) in 100 ml of degassed and anhydrous toluene are charged under argon into a 100 ml test-tube. The 15 orange solution is charged into a Buchi 300 ml glass autoclave, put under 7 bars of ethylene and maintained at room temperature for 1 hour. The autoclave is degassed and the contents discharged without diluting. 1 ml of the solution is removed, 1 ml of a solution of Br<sub>2</sub> in CCl<sub>4</sub> is added 20 and injected into GC: no olefins are present.

Activity: 0 moles of ethylene/V mole

Selectivity: 0% to 1-hexene

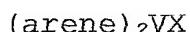
## OLIGOMERIZATION TESTS OF ETHYLENE CATALYZED BY V(I)

	Catalytic precursor (mmoles)	Solvent (ml)	P (bar)	Activity (ethylene moles) / (V mole)	Selectivity (mole %)
4	V(mes) <sub>2</sub> (OCOCF <sub>3</sub> ) (0.089)	Toluene (20)	1	250.5	56
5	V(mes) <sub>2</sub> (OCOCF <sub>3</sub> ) + 2, 5-dimethyl pyrrole (0.2)	Toluene (30)	1	22.26	55
6	V(mes) <sub>2</sub> (OCOCF <sub>3</sub> ) + 2, 5-dimethyl pyrrole (0.138)	Cyclohexane (25)	1	22.54	46
7	V(mes) <sub>2</sub> (BPh <sub>4</sub> ) (0.1)	Toluene (30)	1	29.8	66
8	V(mes) <sub>2</sub> 6%+Cp <sub>2</sub> Fe(BPh <sub>4</sub> ) (4.12.10 <sup>-5</sup> moles)	Toluene (100)	7	605	99
9	V(mes) <sub>2</sub> I (7.17.10 <sup>-5</sup> moles)	Toluene (100)	7	0	0

Tests carried out at room temperature for 1 hour.

CLAIMS

1. A process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene in the presence of a catalyst comprising a vanadium complex having  
5 the formula:



wherein the term arene represents benzene or mono-, di-, or tri-alkylsubstituted benzene, V is a vanadium ion with a low oxidation state, and X is an anion selected  
10 from Cl, Br and I halide ions, or from non-coordinated anions such as  $B(Ar)_4^-$ ,  $AlCl_4^-$ , carboxylates and sulphonates.

2. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according  
15 to the previous claim, characterized in that the reaction is carried out in the presence of a vanadium com-

plex preferably selected from

bis-(mesitylene)-vanadium trifluoroacetate

bis-(mesitylene)-vanadium-tetr phenylborate

20 bis-(mesitylene)-vanadium-iodide

bis-(mesitylene)-vanadium-tetrachloroaluminate.

3. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according to the first claim, characterized in that the reaction  
25 is carried out with the additional presence of a hetero-

cyclic compound.

4. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according to the previous claim, characterized in that the reaction is carried out in the presence of a heterocyclic compound preferably selected from pyrroles, substituted pyrroles, phenanthroline, pyridine.  
5
5. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according to the previous two claims, characterized in that the reaction is carried out in the presence of a heterocyclic compound in a ratio, with respect to the vanadium complex, ranging from 1 to 20.  
10
6. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according to one or more of the previous claims, characterized in that the reaction is carried out in the presence of a solvent selected from aromatic hydrocarbons and aliphatic hydrocarbons.  
15
- 20 7. The process for the preparation of 1-hexene according to the previous claim, characterized in that the reaction is preferably carried out in the presence of a solvent selected from toluene and cyclohexene.
8. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according  
25

to one or more of the previous claims, characterized in that the reaction is carried out at a temperature less than or equal to 150°C.

9. The process for the preparation of 1-hexene according to 5 the previous claim, characterized in that the reaction is preferably carried out at a temperature ranging from

25 to 60°C.

10. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according 10 to one or more of the previous claims, characterized in that the reaction is carried out at a pressure ranging from 1 to 100 atmospheres.

11. The process for the preparation of 1-hexene according to the previous claim, characterized in that the reaction 15 is preferably carried out at a pressure ranging from 1 to 50 atmospheres.

12. The process for the preparation of 1-hexene consisting in effecting the oligomerization of ethylene according to one or more of the previous claims, characterized in 20 that the reaction is carried out for times less than 36 hours.

13. The process for the preparation of 1-hexene according to the previous claim, characterized in that the reaction 25 is preferably carried out for times ranging from 1 to 24 hours.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/02827

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C11/107 C07C2/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 44 36 113 A (HOECHST) 11 April 1996 (1996-04-11) claim 1 -----	

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## ° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

8 May 2001

Date of mailing of the international search report

14/05/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Van Geyt, J

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

In	International Application No
I ..	EP 01/02827

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE 4436113	A 11-04-1996	BR	9504330 A	08-10-1996
		CA	2160101 A	11-04-1996
		CN	1129226 A	21-08-1996
		EP	0707010 A	17-04-1996
		FI	954785 A	11-04-1996
		JP	8193092 A	30-07-1996
		NO	954012 A	11-04-1996
		US	5670436 A	23-09-1997
		ZA	9508487 A	08-05-1996